

***Polyurethane Waste Disposal Process Development: Amine Recovery*****INTRODUCTION**

Due to the increase in the use of thermoset polyurethanes, it became prudent to investigate methods for the economic and ecological recycling of wastes from these processes. Because they are thermoset materials, polyurethanes cannot be ground and injection molded in the same manner that thermo-plastic scrap is recycled.

Investigation in this laboratory proceeded with the following criteria. The process developed should (1) be low pressure, (2) use few chemical additives, and (3) produce useful polyol. A low-pressure superheated steam decomposition technique was developed which satisfied the above criteria, and is discussed in a previous publication.<sup>1</sup> This note describes the techniques which at this point in a continuing developmental effort appear most economical and energy efficient in purifying the reactor condensate and reclaiming the diamine product. The diamine, when reclaimed, can be used to make tolylene diisocyanate, a foam starting material.

**CONTACT SPRAY CONDENSER MODIFICATION**

This note will deal with the process starting at the spray condenser and describe a method for steam purification and diamine recovery. As described in an earlier paper,<sup>1</sup> it was necessary to use a contact spray condenser to avoid condenser fouling early in the decomposition. It was further found that during extended operation, the spray condenser also plugged owing to accumulation of products and contaminants that were insoluble in the steam condensate. The contaminants were found to be partially decomposed ureas and fragments from the acrylonitrile organic filler in the foam. To remedy this, a program of research was instituted to develop a system with an organic-water co-condenser fluid. Many solvents were examined including methylene chloride, chloroform, aniline, and benzyl alcohol. During this screening, several important solvent water parameters became evident. The solvent should have a strong positive temperature solubility characteristic with water. It should have at least a 10-to-1 partition coefficient for the diamine when used as an extractant from water. And finally, the solvent and water should be relatively insoluble at room temperature and have an azeotrope.

Two compounds which had these characteristics were aniline and benzyl alcohol. Both of these compounds were used in the contact condenser, Figure 2. Several ratios of organic solvent to condensate were tried and a ratio of one part organic to four parts condensate was found to be desirable to ensure trouble-free condenser operation. At concentrations below this, the organics were not completely soluble; and if more than the optimum was used, it would cause undue expense of energy when separating the products from the solvent. The operating temperature of the condenser was found to be optimum between 80° and 90°C, which produced a homogeneous, pumpable fluid of

**TABLE I**  
Rectification of Extracts

bp, °C	Aniline extract	Benzyl alcohol extract
95-99	water and aniline codistillate and azeotrope	
99		water-benzyl alcohol codistillate and azeotrope
135/20 torr	aniline	
150/25 torr		benzyl alcohol
110-150/7-9 torr	"Lights" low molecular weight polyols	
160-180/10 torr	diamine cut	
—	residue	

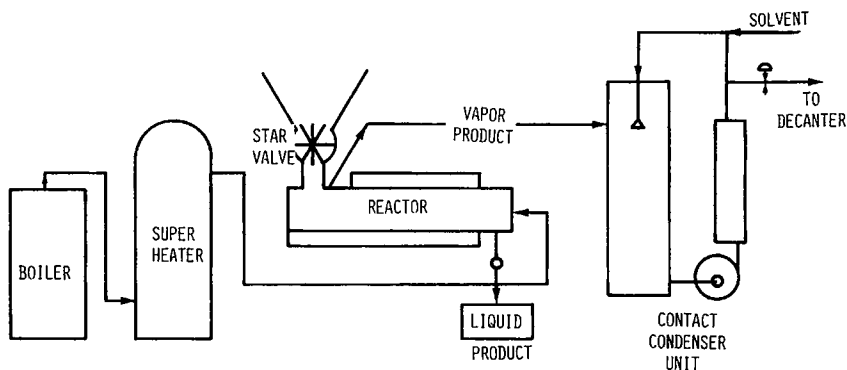


Fig. 1. Reactor complex.

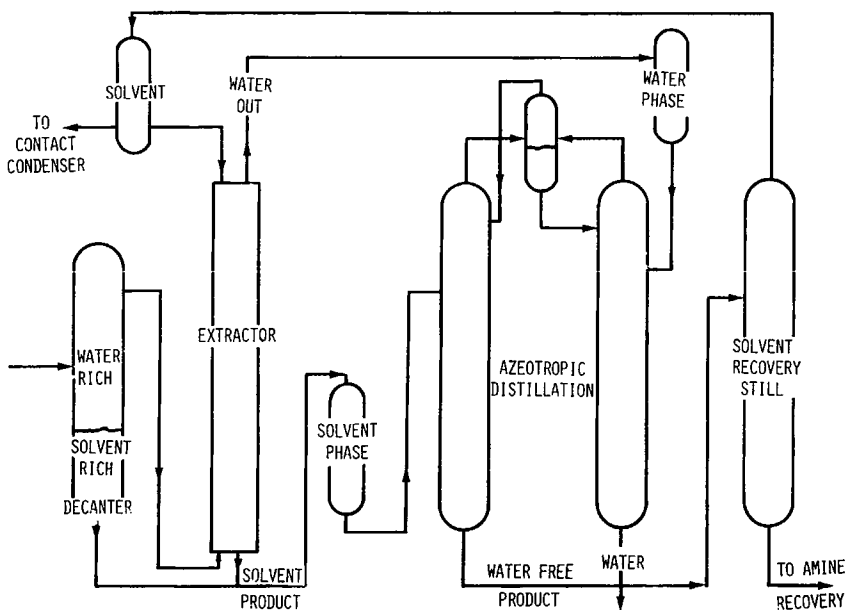


Fig. 2. Solvent-water recovery system.

condensate, solvent, and organic products from the reactor. The condenser fluid is withdrawn at the same rate the reactor condensate and solvent are added. The mixture is then pumped to a holding tank where it is decanted.

### SOLVENT RECOVERY

As discussed earlier, the solvent used in the contact condenser should azeotrope with water. This criterion provides a means for the primary rectification of the diamine product. The azeotrope was found to boil at its predicted temperature with the organic contaminants present in the solvent. The purification is described in Table I for a typical run using aniline and benzyl alcohol as solvent.

In both systems, the spray condenser output is allowed to settle at room temperature. The decanted organic phase is then distilled in stages. First, the solvent-water azeotrope is removed at atmospheric pressure. Succeeding stages of the distillation are carried out under vacuum.

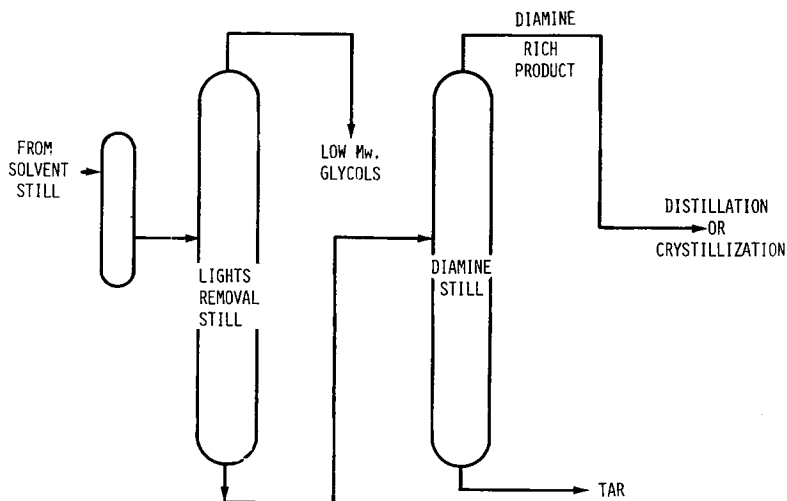


Fig. 3. Amine purification system.

### DIAMINE RECOVERY

Shredded polyurethane foam (2.4 kg) was added portionwise into the reactor countercurrent to flowing steam at 288°C at 1 atmosphere. The steam flow rate was 8 kg/hr. The ratio of water to benzyl alcohol in the spray condenser was maintained at 2:1 v/v. During a 5-hr run, approximately 1.2 kg of polyol was collected from the bottom of the reactor. In the same period of time, 60 liters of condensate was collected from which 20 liters of benzyl alcohol solution was separated. The benzyl alcohol was stripped at 25 torr through a 350 × 35 mm column packed with Raschig rings. The pressure was reduced to 5–10 torr and a crude diamine cut was taken. Subsequent fractional distillation gave, in addition to a forerun of light polyols, 192 g (50% of theory) of tolylene diamines, bp 160–180°C/10 torr, with an isomer ratio of 74/26:2,4/2,6 by infrared determination. NMR spectra and thin-layer chromatography against an authentic sample on silica gel developed with isoamyl alcohol:benzene 1:1 and visualized with phosphomolybdic acid spray offered confirming evidence of the identity of the diamines.

### PROCESS DESIGN

The proposed process can be broken down into three units: the reactor complex, solvent and water recovery, and diamine purification. The reactor complex has the elements shown in Figure 1. Steam would be produced and superheated to 316°C. The steam stream is proposed to be split between the reactor jacket and reaction zone. It is desirable to keep the steam which enters the contact condenser at a minimum flow to reduce the amount of solvent necessary for extraction of the condensate. Thus, as much heat as possible will be added using the reactor jacket. The polyol liquid product will be removed from the reaction zone, cooled, and filtered. At this point, it is ready for use. The vapor product is condensed in the contact spray condenser with continual addition of solvent and removal of the condenser mixture. The output from the spray condenser is delivered to the decanter in the solvent–water recovery section, Figure 2. The water-rich phase is removed from the decanter and extracted with fresh solvent to remove residual product. Then, the water-rich phase is distilled to recover the water to be reused as boiler feed. The solvent-rich phase from the decanter and the extractor are combined and distilled to remove the water.

Subsequently, the still bottoms are fed into the solvent recovery still. The overheads are sent to the solvent storage, and the still bottoms are then delivered to the solvent storage and the still section, Figure 3. The first still removes the low-boiling glycols in the overheads, and the product from the stripping section is distilled to produce the diamine product in the overhead. The still bottoms are tars which can be burned for their fuel value, as can be the glycols from the previous still.

This proposed process meets the objectives of not creating unmanageable waste streams during the polyurethane recovery process. The solvent and water are purified and reused in the process. The only process wastes are high-density materials which have a potential use for their fuel value.

#### References

1. G. A. Campbell and W. C. Meluch, *Environ. Sci. Technol.*, **10** (2), 182 (1976).

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